ISOLATION OF RUTIN FROM CERASUS PSEUDOPROSTRATA

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We have studied the composition of the flavonoids of Cerasus pseudoprostrata Pojark. collected in 1962 in Uzbekistan.

The comminuted branches of C. pseudoprostata were extracted with methanol, the solvent was distilled off in vacuum, and the residue was dissolved in water and transferred to a polyamide column. Elution with water gave a crystalline substance. Yield 0.1%, mp 190.5°–192° C (from 95% alcohol), $C_{27}H_{30}O_{16} \cdot 2H_2O$.

On paper chromatography in the butanol–acetic acid–water (4 : 1 : 5) system, this compound gave a spot with R_f 0.40, and on a plate with a thin layer of polyamide in the methanol–water (8 : 2) and methanol systems it gave spots with R_f values identical with those for rutin (0.41 and 0.40, respectively).

The acid hydrolysis of the substance gave quercetin, glucose, and rhamnose. The sugars were identified by paper chromatography [1] and the quercetin by its IR spectrum, the absence of a depression of the melting point (mp 314° C, decomp.), of a mixture with an authentic sample of quercetin, and also by paper chromatography in a thin layer of polyamide.

Methylation with dimethyl sulfate [1] and subsequent removal of the carbohydrate residue gave 5, 7, 3', 4'-tetramethylquercetin with mp 195°–196° C, which shows the attachment of rutinose to the quercetin in position C_3. Thus, the substance isolated from the leaf-bearing branches of C. pseudoprostrata is rutin, which is confirmed by the absence of a depression of the melting point of a mixture with rutin, and also by the identity of their UV and IR spectra.

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A SESQUITERPENE LACTONE FROM ARTEMISIA JUNCEA

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The leaves and flower heads of Artemisia juncea Kar. et Kir. contain santonin (0.28–0.36%), essential oil (0.28–1.02%), and alkaloids (about 0.1%) [1–3]. The content of santonin was shown by the preparation of the crystalline substance by Massagetov's method developed for santonin. The identification of this substance with an authentic sample of santonin has not been carried out.

To study the lactones of the plant concerned, we investigated samples collected on the 25th June, 1964, at the beginning of the budding period (Kuyuk Pass). From the leaves and flower heads we isolated by a method described previously [4] a substance of the composition $C_{15}H_{18}O_4 \cdot H_2O$ (from alcohol), mp 149°–150.5° C in a yield of 0.2%.

To eliminate water of crystallization, this substance was dried at 130° C for 6 hr; the melting point remained unchanged, and so did the IR spectrum.

Found, %: C 68.96, 69.08; H 7.03, 7.01; mol. wt. 265.2 (Rast). Calculated for $C_{15}H_{18}O_4$, %: C 68.71; H 6.87; mol. wt. 262.

The IR spectrum of the substance had absorption bands at 3550 (OH group), 1683 (α, β-unsaturated ketone), 1621, 1641 (C=C bond) and 1771 cm^{-1} (absorption band of a carbonyl group of a γ-lactone ring). The UV spectrum, λ_{max} 256 mμ (log ε 4.14), shows the presence of a conjugated system. The substance obtained forms an acetyl derivative with mp 190°–191.5° C and the composition $C_{17}H_{20}O_5$.

The constants of the substance considered agree completely with the results for deacetylmatricarin, a sesquiterpene lactone isolated previously from A. tilesii, A. austriaca, and A. lercheana [5, 6], which was confirmed by paper and thin-layer chromatography and a comparison of the IR spectra of mixtures with an authentic sample of deacetylmatricarin.

Thus, the leaves and flower heads of Artemisia juncea contain the sesqiterpene lactone deacetylmatricarin. Santonin was not found in this plant.

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THE STRUCTURE OF MERISTOTROPIC ACID

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The triterpene hydroxyketoacid (I) of composition $C_{32}H_{48}O_4$, $[\alpha]_D$ −67° C, called meristotropic acid has been found in the roots of Meristotropis xanthoides Wass. The ketone group of this acid is unreactive; judging from the ease of saponification of the methyl ester the carboxyl does not suffer much steric hindrance; the absorption in the UV region shows the presence of a conjugated diene [1].

Data	Substance	Mp, ° C	$[\alpha]_D$, deg	Absorption in the UV spectrum
Hour results	(VIII)	222—224	—120	—
	(IX)	227—228	—170	λ_{max} 278 mμ (log ε 3.9)
Reference [6]	(VIII)	229	—	—
	(IX)*	233—234	—168	λ_{max} 277 mμ (log ε 4.12)

From the plant mentioned we have isolated meristotropic acid (I) with mp 358° C, λ_{max} 242, 250, 258 mμ (log ε 4.38, 4.43, 4.34, and have obtained derivatives of it: methyl ester (II) with mp 278 ° C, acetate of the methyl ester (III) with mp 248° C, triol (IV) with mp 230° C, λ_{max} 244, 252, 260 mμ (log ε 4.34, 4.39, 4.18), and its triacetate (V) with mp 238°–240° C, deoxymeristotropic acid, (VI), with mp 323° C, its methyl ester (VII) with mp 235°–237° C, $[\alpha]_D$ −125° C, λ_{max} 242, 250, 260 mμ, and the acetate of the methyl ester (VIII) with mp 222°–224° C, $[\alpha]_D$ −120° C.

Substance (IV) was obtained by reducing (II) with lithium aluminum hydride, and (VI) by reducing (II) by Nagati and Itazaki's method [2]. The other substances were prepared by the usual methods. The analysis of six of these compounds led to the formula $C_{30}H_{44}O_4$ for meristotropic acid. This formula, the high negative rotation $[\alpha]_D$, and the characteristic absorption in the UV region of all the compounds investigated permit the conclusion that meristotropic acid has the hydrocarbon skeleton of oleana-11, 13(18)-diene. The hindered ketone group cannot be located at C_3, and since all the natural compounds of the oleanane group with an unbroken carbon skeleton have an oxygen atom at C_3, there must be a hydroxyl in this position. The acetylation of the methyl and ethyl esters of (I) [1] and also of substance (VII) lead to practically no change in $[\alpha]_D$. Consequently, the hydroxyl is in the equatorial position (the acetylation of (I) took place anomalously in our experiments). The carboxyl cannot be at C_4 because the triol does not form an acetonide. It may occupy position 28 or 30: such compounds are known [3, 4] and are different from deoxymeristo-

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* This sample melted at 229°–230° C in our experiments; a mixture with the dienedione (IX) from meristotropic acid had mp 228.5°–229.5° C.